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Technical Note

Electrochemical impedance spectroscopy: A deeper and quantitative insight into the fingermarks physical modifications over time

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ABSTRACT

The present work is focused on a novel approach for the study and quantification of some of the physical changes to which a fingermark deposited on non-porous substrates is subjected as its ageing proceeds. Particularly, electrochemical impedance spectroscopy (EIS) technique has been applied for the first time in order to monitor the electrochemical behaviour of the system constituted by the fingermark residue and the underlying substrate. The impedance spectra proved to be significantly affected by the presence of the mark residue as well as by its ageing process. Opportune fitting operations performed on the experimental data allowed obtaining quantitative electrochemical parameters used to reach useful information on the fingermarks ageing mechanism as well as to calculate the fingermark ageing curves from which fundamental information could be potentially extrapolated.

1. Introduction

Fingermarks found at the crime scene undoubtedly represent one of the most important forms of physical evidence of paramount forensic relevance. Although significant progresses have been achieved in recent years in the field of latent fingermarks development, as a result of astonishing advancements in the field of nanotechnology [1–4], as well as in immunological detection techniques [5–7], there is still increasingly need for enhancements in sensitivity and specificity, as recently underlined by several researchers [8,9], in order to reduce the number of fingermarks remaining undetected.

Moreover, it is well recognised how the probative potential of fingermarks is still significantly under-expressed, as a result of the lack of reliable methodologies for fingermark age determination [10], the latter representing one of the grand challenges for future forensic sciences innovation [11], since it would allow discriminating between traces effectively related to the criminal activity and those which are, instead, legitimately present at the crime scene.

It is beyond a shadow of a doubt that the above mentioned issues related to both latent fingermark detection and fingermarks age determination, would benefit from a deeper understanding of the ageing process of the mark itself, with the present study aiming at partially addressing that topic.

The ageing of fingermark traces is a tremendously complex phenomenon, which is affected by a huge number of factors including fingermark composition, nature of the substrate and environmental conditions, together with their mutual interactions as well described by the Triangle of Interaction [12].

Research efforts during recent years were directed toward the study of both chemical [13–19] as well as physical [20–23] modifications encountered by the fingermark as the time proceeds. Indeed the chemical modification/decomposition process of the complex mixture of organic as well as inorganic compounds, resulting from the secretions released by eccrine and sebaceous glands [24], is accompanied by morphology variations, like changes into the ridges width and thickness, as well as their loss of continuity, together with an increase into the pore size [8,20–22,25]. Although, the optimum method for potential fingermarks age determination has recently been recognised [10,26] as necessarily based on the exploration of changes to fingermark chemical constituents over time through comparison of parent compounds and degradation products, the possibility to support those modifications by concurrently monitoring the morphological-physical ones occurred in the fingermark aged over a particular substrate would be undoubtedly an added value, particularly if the latter could be objectively quantified. Indeed, up to now, the above mentioned physical modifications of a fingermark undergoing an ageing process (both before and after the application of a fingermark detection technique), have been mainly monitored

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Table 1
Characteristics of the two donors considered and the number of the fingermarks deposited for the present study.

Donor	Sex	Age	Race	Number and type of marks deposited	Substrate	Recent skin product use
1	Male	36	Caucasian	2 groomed 4 natural	Stainless steel Stainless steel, brass	No
2	Male	40	Caucasian	1 groomed 1 natural	Stainless steel Stainless steel	No

by microscopy techniques, and attempted to be quantified by image analysis, significantly limiting the sensitivity of the methods proposed to the resolution of the resulting micrograph or of the microscope employed, and more easily exposing the results to the subjectivity of the researcher/operator.

The aim of the present work is to propose for the first time the use of electrochemical impedance spectroscopy (EIS) as a potential complimentary technique for the monitoring and quantification of some of the physical changes to which fingermarks deposited on metallic substrates are subjected. The present study also allows reaching a deeper understanding of the fingermark ageing mechanism (limited to non porous metal substrates) going beyond the limits imposed by microscopy observations.

2. Materials and methods

2.1. Fingermark samples

The results presented in this work are referred to a limited number of two donors, since the study was aimed at demonstrating and confirming the possibility to use EIS technique in monitoring and quantifying some of the fingermarks physical modifications over time, rather than being thought for a comparison between the obtained ageing trends. The characteristics of the donors together with the number and the type of fingermarks deposited are reported in Table 1.

Being EIS an aqueous solution based technique, thus potentially sensible to water insoluble components of the fingermark residue, its applicability was initially tested on sebaceous marks, for the deposition of which the donor was asked to gently rub his fingers on his forehead before touching the substrate.

However, as recently recommended by the International Fingerprint Research Group (IFRG) [27], the here presented methodology was investigated also on ungroomed "natural" fingermarks in order to be representative of a real scenario. For this latter collecting procedure, the donors were asked not to wash their hands for at least 60 min before deposition, as well as to rub their hands together before deposition, in order to homogenise the mixture of eccrine and sebaceous secretions already present on their skin.

Fingermarks were deposited on two different metallic substrates, namely AISI316L stainless steel and commercial yellow brass (65 wt% Cu and 35 wt% Zn), without controlling the applied pressure and the deposition time. These substrates were selected due to their widespread utilisation in a huge number of household furnishings. Moreover the composition of the selected brass is very close to the brass typically employed for cartridges manufacturing.

The metal substrates bearing the latent marks were stored in the laboratory at average values of storage temperature and relative humidity of 25 °C and 45% RH respectively.

2.2. Electrochemical impedance spectroscopy (EIS) experiments

Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and then measuring the current through the cell; like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current, but unlike resistance, it is not limited by the simplifying properties of an ideal resistor (i.e. to follow the Ohm's Law at all current and voltage levels, to have resistance value independent of frequency and to have AC current and voltage signals always in phase with each other). By assuming to apply a sinusoidal potential excitation: the response to this potential is an AC current signal. This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series). An expression analogous to the Ohm's Law allows calculating the impedance, Z, of the system at a fixed frequency as the ratio between the AC applied potential (expressed as sinusoidal function) and the response AC current (expressed as sinusoidal function), as showed in Eq. (1).

$$Z(\omega) = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (1)$$

Usually the impedance is therefore expressed in terms of a magnitude, Z_o (obtained as the ratio of the amplitudes of potential and current sinusoidal functions), and a phase shift, Φ (phase shift between the AC potential input and the AC current output).

An impedance spectra is obtained when a number of impedance measurements are carried out at different frequencies; impedance spectra are usually plotted in graphs that show the change of both the magnitude (Z_0) and phase (Φ) with the frequency (Bode plots).

Using the Eulers relationship it is possible to express the impedance as a complex function: for each frequency the impedance will be represented by a pair of values, a real part, Z_{real} and an imaginary part, Z_{imm}. With this representation impedance spectra are usually plotted in graphs that show the change of both the real (Z_{real}) and imaginary (Z_{imm}) parts with the frequency (Nyquist plots). The analysis of impedance spectra can provide information about the electrical conductivity changes which may occur at different frequency in materials, electrochemical systems and electrified interfaces. In this work the variation of the impedance of the system 'metal + fingermark' occuring during the ageing process of the fingermark was investigated.

Particularly, a three electrodes cell (Flat Cell Model K0235, Princeton Applied Research, Oak Ridge, USA) was employed for the EIS measurements, using the metallic substrate bearing the fingermark as working electrode, a platinum foil as counter electrode and Ag/AgCl/KCl_{sat} as reference electrode. As schematically depicted in Fig. 1, the cell consists of a glass cylinder clamped horizontally between two end plates. One end plate houses the working electrode and the other houses the counter electrode. The reference electrode is housed in a Luggin well, with a fixed Teflon Luggin capillary protruding from the bottom of the well [28]. Four threaded rods secure the end plates to the glass cylinder. A Viton™ gasket on each end plate seals the plate to the cylinder, preventing electrolyte solution, i.e. 0.2 M Na_2SO_4 (≥99.0%, Sigma Aldrich, Milan, Italy), from leaking.[1] A Teflon gasket exposes 1 cm^2 area of the working electrode to the cell solution. In the present study the working electrode was positioned so that the exposed area was the one in correspondence of the central region of the fingermark, and

[1] Na_2SO_4 aqueous solution was chosen as electrolyte since it ensures an adequate conductivity while keeping the pH neutral and avoiding strong corrosive reactions with the metallic substrates selected.